LBL-10941
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

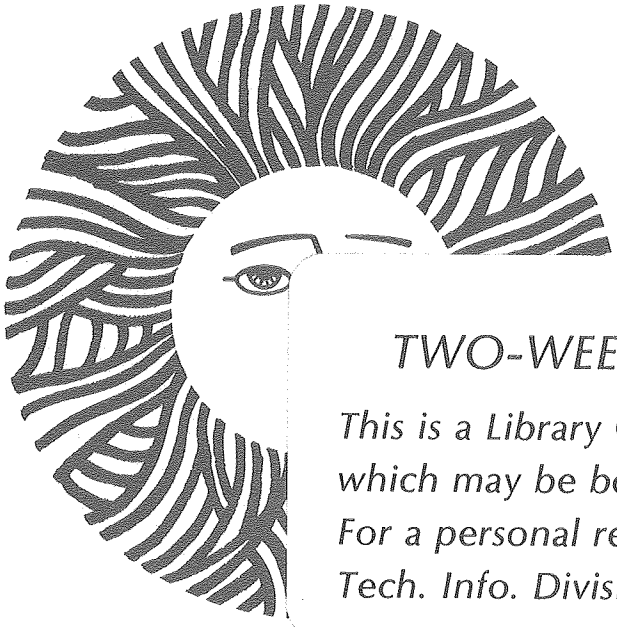
ENERGY & ENVIRONMENT
DIVISION

Submitted to the Journal of Fire Materials

A COMPUTATIONAL STUDY OF PHYSICAL AND CHEMICAL INHIBITION IN A PERFECTLY STIRRED REACTOR

Nancy J. Brown and Robert W. Schefer

May 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

A COMPUTATIONAL STUDY OF PHYSICAL AND CHEMICAL INHIBITION IN A PERFECTLY STIRRED REACTOR

Nancy J. Brown
Robert W. Schefer

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

This paper reports a set of modelling studies that were undertaken to acquire a more detailed knowledge of combustion inhibition mechanisms. Mixtures of $H_2/O_2/Ar$ reacting in the idealized perfectly stirred reactor were investigated. Three H_2/O_2 kinetic mechanisms were considered, differing from one another by the number of HO_2 reactions included. Two physical inhibitors, Ar and N_2 and one chemical inhibitor, HBr, were investigated. Additional parameters considered were pressure, equivalence ratio, inhibitor concentration and rate coefficient variation. The most effective inhibitor was HBr which acted chemically and caused substantial reduction in radical concentrations in the mixtures considered. The molecules Ar and N_2 acted as physical diluents with N_2 the more effective of the two due to its larger heat capacity.

Research partially supported by the National Bureau of Standards, Center for Fire Research under Grant No. NBS-G7-9006 and by the U.S. Department of Energy, Basic Energy Sciences Division under Contract No. W-7405-ENG-48.

1. INTRODUCTION

Flame inhibitors are broadly classified as being either of the physical or chemical type. The former type is believed to act simply as a physical diluent while the latter is thought to participate directly in the reaction mechanism important to flame propagation. Although no general consensus exists regarding the mechanism(s) of chemical inhibition (1), it is recognized that certain molecules have been observed to retard flame propagation out of proportion to their thermal influence. This leads to the supposition that this type of inhibition is directly linked to chemical reactivity. It must be recognized, however, that the classification of physical versus chemical is largely a matter of degree. Certainly any species added to a combustion mixture which acts as a thermal diluent and is "non-reactive" effects the chemistry indirectly by altering the temperature field. Conversely, chemical inhibitors can act physically by effecting the temperature field of combustion mixtures.

There is a large body of literature associated with flame inhibition studies which are summarized in excellent reviews. Friedman and Levy (2) presented an early survey of proposed extinguishment mechanisms, and recent reviews have been conducted by Creitz (3) and Hastie (4). The most recent collection of papers germane to the subject can be found in (1). A survey of the literature reveals that a wide variety of conditions have been employed in inhibition studies, and that it is not possible to formulate a generalized mechanism which can explain the various results.

This paper reports a set of modelling studies that were undertaken to acquire a more detailed knowledge of combustion inhibition mechanisms. Mixtures of $H_2/O_2/Ar$ reacting in the idealized perfectly stirred reactor are investigated. Three H_2/O_2 kinetic mechanisms are considered,

differing from one another by the number of HO_2 reactions included. Two physical inhibitors, Ar and N_2, and one chemical inhibitor, HBr, are studied. Parameters considered in the study are pressure, equivalence ratio, inhibitor concentration and rate coefficient variation.

Part two of the paper describes the formulation of the perfectly stirred reactor equations and presents the chemical mechanisms and kinetic data used. Results are presented in part three of the paper. The blowout residence time which is the minimum residence time permissible for stable combustion in the reactor, is found to be especially sensitive to the set of parameters considered here. In addition, hydrogen/oxygen radical pool concentrations and temperature as a function of residence time in the reactor are examined. Heat release rates and reaction rates are also determined at a series of residence times corresponding to stable combustion in the reactor to obtain additional mechanistic information. A comparison of the various inhibitors is given in part four and the mechanistic details of inhibition of $H_2/O_2/Ar$ combustion in a perfectly stirred reactor are discussed.

2. THE MODEL

Extraction of mechanistic information is facilitated by investigating combustion regimes that are strongly dominated by either chemistry or fluid mechanics. Since this work is directed toward gaining an improved understanding of the chemical mechanism of inhibition, the configuration of the chemically dominated perfectly stirred reactor is especially attractive and has been selected for study.

A brief description of the perfectly stirred reactor and the governing equations describing a combustion process in this system are given in this section. The section is concluded with a presentation and discussion of three H_2/O_2 mechanisms and the HBr mechanism used in this investigation.

2.2. The Perfectly Stirred Reactor

The idealized well stirred reactor is a constant volume steady flow reactor in which mixing of the cold incoming gas and the reacting mixture in the reactor occurs instantaneously. Thus, the composition within the reactor is homogeneous and the process is kinetically controlled. The governing equations, using the notation of Jones and Prothero (5) are given below.

The equation describing conservation of energy is

$$\sum_{i=1}^{I} \sigma_i^* h_i - \sum_{i=1}^{I} \sigma_i h_i = \frac{\dot{Q}}{\dot{m}} \qquad (1)$$

where σ_i^* and σ_i are the concentrations of the ith species (mole/gm) at the reactor inlet and exit, respectively. The species enthalpy is designated by h_i; $\dot{Q}$ is the rate of heat loss from the system which is zero for this study, and $\dot{m}$ is the total mass flow rate through the reactor.

The chemistry enters into the reactor description through species conservation equations of which there are I in number.

$$\frac{\dot{m}}{V}(\sigma_i^* - \sigma) = \sum_{j=1}^{J} (\alpha'_{ij} - \alpha''_{ij})(R_j - R_{-j}) \qquad (2)$$

$$i = 1, 2 \ldots I$$

where α'_{ij} and α''_{ij} are, respectively, the stoichiometric coefficients for the ith species in the jth forward and reverse reactions as defined by the general reaction for the species S_i.

$$\sum_{i=1}^{I} \alpha'_{ij} S_i + \bar{\alpha}_j M = \sum_{i=1}^{I} \alpha''_{ij} S_i + \bar{\alpha}_j M \qquad (3)$$

$$j = 1, 2 \ldots J$$

Here $\bar{\alpha}_j$ denotes the stoichiometric coefficient of the third body M and J is the total number of reactions considered in the system. The forward, R_j, and reverse, R_{-j}, reaction rates of the jth reaction, are expresses as:

$$R_j = k_j(\rho\sigma_M)^{\bar{\alpha}_j} \prod_{i=1}^{I} (\rho\sigma_i)^{\alpha' ij} \qquad (4a)$$

$$j = 1, 2 \ldots J$$

$$R_{-j} = k_j(\rho\sigma_m)^{\bar{\alpha}_j} \prod_{i=1}^{I} (\rho\sigma_i)^{\alpha''_{ij}} \qquad (4b)$$

$$j = 1, 2 \ldots J$$

where σ_m is total concentration $\frac{\text{total moles}}{\text{gm}}$ in the reactor and k_j is the Arrhenius rate coefficent of the form

$$k_j = 10^{B_j} T^{N_j} \exp\left(-E_j/RT\right) \quad . \qquad (5)$$

The reverse rate coefficient is obtained from the forward value and the equilibrium constant.

The perfectly stirred reactor equations were solved using a modification of the Pratt-Bowman program (6) which is based upon an accelerated Newton-Raphson algorithm. With a series of residence times which correspond to stable combustion in the reactor as the independent variable, the corresponding compositions and temperatures between the blowout condition and thermodynamic equilibrium were determined from the solution of equations (1) through (3).

2.3 The Chemical Mechanism

The hydrogen/oxygen flame system was selected for study since the kinetics of this system are the best established of any combustion system and are an important subset of the various kinetic schemes governing the combustion of hydrocarbons. An update review (since Baulch, et al. (7)) was undertaken to determine a mechanism and appropriate rate data for the hydrogen/oxygen system. The rate data associated with the three H_2/O_2 mechanisms are shown in Table I. Mechanism I consists of reactions (1) through (7), mechanism II contains reactions (1) through (9), and III is the full set of hydrogen/oxygen reactions (1) through (13). Much of the kinetic data associated with the HO_2 reactions is estimated and is taken from the review of Lloyd (12). The reactant HO_2 is difficult to generate without other radicals being present so that single elementary reactions of HO_2 cannot be isolated for study. It therefore

appeared prudent to segregate the hard kinetic data (Mechanism I) from those containing estimates (Mechanisms II and III). Since third body efficiencies appear better determined for argon as third body than other molecules, argon efficiencies were used throughout for thermolecular reactions. The HBr kinetic mechanism and rate data are also given in Table I. The halogen kinetics have been discussed in detail in a review article by Brown (14).

3. RESULTS

A perfectly stirred reactor can be viewed as a reactor in which stable combustion can occur when volumetric mass flow rates vary between the minimum value associated with full thermodynamic equilibrium in the reactor and that associated with the maximum throughput corresponding to the blowout condition. If the throughput exceeds that at blowout, chemical heat release rates are not great enough to sustain stable combustion. It is our contention that the blowout parameters are especially sensitive to inhibitor type and concentration.

The results of the various calculations are presented in this section. For most of the mixtures considered, a standard mix of 50 percent combustibles and 50 percent argon was considered, with the inhibitor added to the mixture to give mole fractions of inhibitors ranging between 0.02 and 0.10. Since inhibition effectiveness appears to be pressure dependent, calculations were performed at pressures of 0.01 and 1.0 atmospheres using both mechanisms I and III of the $H_2/O_2/Ar$ scheme. The cases of Ar and N_2 inhibition were investigated for stoichiometric mixtures and the case of HBr inhibition was examined for mixtures of equivalence ratios, ϕ = 0.5, 1.0, and 1.5. Results are tabulated in terms of the temperature T, at the blowout condition, residence time , t at blowout , oxygen consumption during the blowout residence time and a type of inhibition parameter θ_t which is defined as:

$$\theta_t = \left(\frac{t - t^\circ}{t}\right)\frac{(O_2)}{(I)} \qquad (5)$$

where t° and t are respectively, the blowout residence times of the uninhibited and inhibited mixtures. The residence time ratio is multiplied by the amount of molecular oxygen consumed during the blowout

residence time and divided by the concentration of inhibitor in the mixture. Implicit in using this parameter to characterize inhibition is the assumption that molecular oxygen consumption is directly related to the branching process and is therefore related to combustion stability. The ratio $(O_2)/(I)$ does remove some of the composition dependence of the inhibition parameter. The parameter θ_t is somewhat analogous to the parameter ϕ_ν suggested by Fristrom and Sawyer (17) to describe inhibition in premixed flames. The analogy is, however, imperfect since the relationship between blowout residence times and flame speeds is complex.

An additional way to characterize inhibition is to examine the effects of the inhibitor type and concentration on radical concentrations. The total hydrogen/oxygen radical pool concentrations were plotted as a function of reactor residence time between the blowout and equilibrium residence times. To facilitate comparison and to partially account for dilution by the various inhibitors, the pool concentrations were normalized by the maximum possible pool function for a given mixture, that is the quantity

$$Z = \frac{n_H + n_O + n_{OH} + n_{HO_2}}{2n^i_{H_2} + 2n^i_{O_2} + n^i_{HBr}} \qquad (6)$$

was computed at each residence time where n_i is the number of moles/g of the species i in the mixture, and the superscript i designates the initial concentrations of reactants in moles/g.

3.2 Comparison of the Various H_2/O_2 Mechanisms

It is important to understand the effects of the HO_2 reactions on the blowout characteristics of the $H_2/O_2/Ar$ mixture before discussing

inhibition effects. Figures 1 and 2 are, respectively, plots of blowout residence time versus equivalence ratio for mixtures reacting at 0.01 and 1.0 atmosphere pressure. The curves are parabolic in shape and are thus typical blowout curves. The residence times at the lower pressure are approximately 500 times less than at atmospheric pressure. Correspondingly, the temperatures at blowout are approximately 250 to 275 K less at the lower pressure. This behavior can be attributed to the relative increased importance of the thermolecular reactions at the higher pressure. These reactions contribute substantially to the net chemical heat release rates and thus account for the increased temperatures and decreased residence times of the atmospheric pressure cases.

Examination of the two figures reveals that the blowout characteristics are nearly identical for Mechanisms II and III. This is so since reactions (8) and (9), the only HO_2 reactions of Mechanism II, are the dominant HO_2 reactions of Mechanism III. Mechanism II is eliminated for further consideration since the difference between the two mechanisms is small.

The low pressure mixtures exhibit less variation with respect to mechanism than mixtures reacting at one atmosphere since HO_2 formation rates and subsequent HO_2 reaction rates are substantially reduced at the lower prssure. The differences with respect to mechanism decrease with increased equivalence ratio since HO_2 formation and reaction rates are greatest for the lean flame and vary inversely with equivalence ratio. The higher temperatures and lower residence times associated with Mechanism III relative to Mechanism I calculations are due to the contribution of the HO_2 formation reaction to the overall heat release rate in competition with the endothermic $H + O_2$ branching reaction.

The subsequent exothermic reaction of HO_2 via reaction (9) to generate OH which then reacts exothermically via (2) tends to further increase the heat release rates which in turn results in the increased temperature and decreased residence times at blowout.

3.3. Blowout Characteristics

The blowout characteristics of the argon inhibited stoichiometric mixtures are summarized in Table II. The residence time increases with increasing inhibitor concentration and the temperature decreases by approximately one degree per 0.02 mole fraction increase of argon. The molecular oxygen consumption exhibits a slight increase with inhibitor concentration and more oxygen is consumed for the atmospheric pressure mixtures. The inhibition parameter varies slightly over the range of variables considered and tends to increase with: 1) decreased inhibitor concentration, 2) Mechanism I, and 3) increased pressure. The characteristics of a mixture inhibited with molecular nitrogen are similar and somewhat more exaggerated; for instance, under identical conditions, θ_t is greater for N_2 than Ar. Table III summarizes the results of the N_2 inhibition calculations.

Inhibition by HBr was investigated as a function of HBr concentration, equivalence ratio, hydrogen/oxygen mechanism, and pressure. The behavior of these mixtures at the blowout condition is summarized in Tables IV, V, and VI. It is of interest to examine how the variables: residence time, temperature, O_2 consumption and θ_t behaved with respect to variations in the input conditions. Individual reaction and heat release rates have also been examined at the blowout condition for the reactions listed in Table I.

The residence time, temperature and O_2 consumption increase with increasing HBr concentration. The inhibition parameter θ_t also increases with HBr for mixtures at one atmosphere pressure. The effect of increasing the HBr concentration on the various reaction rates and the net heat release was also examined. The heat release rate for the individual reactions listed in Table II was determined by multiplying the enthalpy in the forward direction by the difference of the forward and reverse reaction rates. The net heat release rate for the entire set of reactions was obtained by summing the contributions for the individual reactions. The net heat release rate was, of course, negative since the reaction sequence generates heat. The absolute value of the net heat release rate decreased with increasing HBr, that is, less heat was generated per unit time. The fraction of the net heat release rate contributed by the HBr reactions (14) through (17) increased with HBr concentration. It may appear unusual that the temperature increases with HBr concentration while the net heat generated per unit time decreases. These are consistent since the important quality in raising the temperature of a mixture is the net heat generated, and this increases since the residence time increase more than compensates for the decrease in the heat generated per unit time. The increased residence time is also responsible for the increased O_2 consumption and compensates for the decreased rates of O_2 consuming reactions that were observed.

The effect of pressure on HBr inhibited mixtures can be determined by comparing cases where all input variables except pressure are identical. As pressure is increased, temperature, O_2 consumption, and θ_t increase. Residence time decreases with pressure and the absolute value of the net heat release rate increases due to the increased importance of the exothermic termolecular reactions. These effects are similar to those observed for Ar and N_2 inhibited mixtures.

The inhibition parameter θ_t (with a few exceptions) and the temperature of the mixture at blowout increases with equivalence ratio. Temperature and the inhibition parameter are greater for mixtures reacting via Mechanism III. Residence times and O_2 consumption are less for mixtures reacting via Mechanism III than those reacting via Mechanism I.

3.4 Radical Profiles

Radicals are rapidly shuffled back and forth by a series of bimolecular reactions so that it appeared more reasonable to examine total radical concentration than individual ones. The reduced radical pool concentration, Z, defined in Eq. (6) was used to ascertain the effects of the different input variables on radical concentrations. The quantity Z is the ratio of the hydrogen and oxygen containing radical species to the maximum concentration of hydrogen and oxygen containing radical species possible for a given mixture. The maximum concentration was determined by assuming that all the initial H_2, O_2 and HBr dissociated to form radical species. The quantity Z was calculated for a series of residence times in the reactor which corresponded to stable combustion, and pool profiles were determined by plotting Z as a function of residence time.

The dependence of Z on inhibitor type and concentration, pressure, equivalence ratio, and mechanism is illustrated in figures 3 through 7. The profiles shown in these figures have a similar shape. The value of Z at the blowout residence time increases and assumes a maximum value at a time slightly greater than blowout, then declines slowly (especially at 0.01 atmospheres) to the final thermodynamic equilibrium value.

Figures 3 and 4 are plots of Z as a function of residence in the reactor for 2 and 10 percent argon and hydrogen bromide, respectively. A slight decrease in Z with increasing argon occurs; however, a substantial decrease in Z is evident for hydrogen bromide addition. The effect of nitrogen addition on Z is similar to that noted for argon. It is important to examine the effect of the term n_{HBr} in the denominator of Equation (6) on Z for the cases of HBr addition. Eliminating the term increases the 10 per cent curve by 1.1. relative to the 2 per cent curve; however, the difference between the two curves; though somewhat reduced, remains substantially greater than that observed for physical inhibitors.

The effect of pressure on the Z profile is illustrated through a comparison of Figures 4 and 5, which are plots of Z versus residence time for two concentrations of HBr at two pressures. There are more radicals at the lower pressure and HBr is more effective in reducing Z at times near blow-out for the mixture at atmospheric pressure.

The effect of equivalence ratio on the Z profile is illustrated through comparison of Figures 5 and 6. Radical fractions are largest for the stoichiometric flame; however, the decrease in Z with HBr addition increases with equivalence ratio.

The effect of mechanism on Z is illustrated in Figure 7. The intersection of the curves at relatively short times is characteristic of the several cases considered. At the blow-out condition, Z was greater for mechanism III than I; however, at times close to the maxima in the III curves, the Z profiles intersect and the order is reversed. This trend is most exaggerated for the lean mixture shown in the figure since the difference between the two mechanisms with regard to blow-out residence time and θ_t was greatest for the lean mixture.

4. DISCUSSION

Argon and nitrogen behave similarly with regard to their inhibition characteristics. The addition of these inhibitors slightly lowers the temperature of the blowout condition and radical pool concentration and increases the residence times and the oxygen consumption. These inhibitors act as thermal diluents since they use a portion of the chemical heat release to raise their temperature and, in so doing, effectively lower the temperature of the overall mixture. This, in turn, results in lowered reaction rates and consequent reduced heat release rates, and thus requires longer residence times (or conversely, reduced mass flow rates) in the reactor.

Larsen (18) has maintained that the primary role of halons in flame suppression is as heat sinks, and that they have a common mechanism with inert gases. Furthermore, Larsen suggests that one should consider inhibitors on the bases of their weight percent in the total mixture. A series of calculations nearly identical to the third group in Table V were performed to investigate Larsen's premise. The rate coefficients of reactions (14) through (17) were set equal to zero for these calculations, and the results were nearly identical to the analogous case for nitrogen inhibition, and not to those given in Table V. Hydrogen bromide only acts as an inert for the unrealistic case of zero reactivity. Furthermore, for this case, it behaves identically to nitrogen on a molar, not weight, basis.

Hydrogen bromide is a different kind of inhibitor than argon and nitrogen. Evidence that it acts chemically is provided by the substantial decrease in the radical pool with increased hydrogen bromide concentration. The temperature increase at the blowout condition is another indication that hydrogen bromide acts chemically since thermal diluents result in lower rather than higher temperatures at the blowout condition.

If residence time increase is used as the criterion for inhibitor ranking, hydrogen bromide is the most effective inhibitor for all mechanism III calculations; however hydrogen bromide is less effective than nitrogen for mechanism I calculations at 0.01 atmospheres, but is more effective at atmospheric pressure. This latter result is illustrated in Figures 8 and 9 where residence time at blowout is plotted versus inhibitor concentration at 0.01 and 1.0 atmospheres, respectively.

Using the parameter Θ_t as a basis for comparing the three inhibitors reveals that hydrogen bromide is the most effective inhibitor for the entire set of variables considered. Comparison of the various hydrogen bromide cases reveals that inhibition is more effective for mechanism III than I and increases with pressure and equivalence ratio. Dixon-Lewis and Simpson (19) found that HBr was more effective in rich $H_2/0_2/N_2$ flames and that effectiveness increased with pressure. Rossner et al (20) found bromide inhibitors to be more effective in rich methane/air rather than in lean mixtures which also concurs with the observed dependence of inhibitor effectiveness on equivalence ratio noted here.

Examination of the HBr reaction and heat release rates revealed that the reverses of reactions 14 and 17 (14r and 17r), are responsible for the inhibitory action of hydrogen bromide. This concurs with the conclusions of Fristrom and Van Tiggelen (21) and Dixon-Lewis and Simpson (19). Reactions (14r) and (17r) are both exothermic with the latter a factor of five more exothermic than the former. Both reactions scavenge hydrogen radical and thus reduce hydrogen/oxygen pool radicals. Reaction (14r) is approximately twenty times faster than (17r) at .01 atmosphere, while at one atmosphere it is four to ten times faster thereby having a comparable heat release rate.

It is our contention that the variation of Θ_t with hydrogen bromide concentration is a manifestation of the complex trade-off between the radical scavenging ability and exothermicity of the important inhibitor reactions. Rate coefficient variation of reaction (17) provides additional evidence in support of this contention. These results are summarized in Table VII. No rate coefficient variation is associated with case A which is computed with the kinetic data of Table I. The forward and reverse rate coefficient of reaction 17 is multiplied by zero for case B and by 100 for case C. Neglect of reaction (17) results in lower blowout temperatures. The parameter Θ_t is greater for case B than A, and is nearly constant. Increasing (17r), results in larger blowout temperatures and residence time as a function of hydrogen bromide concentration has a minimum at a mole fraction of .02. The only concentration of hydrogen bromide yielding a positive Θ_t is a mole fraction of 0.10. In other words hydrogen bromide would be a promoter rather than an inhibitor, if reaction 17 were accelerated by a factor of 100. Comparison of cases A through C, illustrates that reaction ^{14r} is the primary one responsible for hydrogen bromide inhibition since it has relatively greater radical scavenging ability for less exothermicity. Furthermore, the parameter Θ_t would be a more reasonable parameter if the complex trade-off between exothermicity and radical scavenging especially manifest by reaction (17r) did not exist.

The increase in Θ_t with equivalence ratio and with mechanism III over mechanism I is consistent with the preceding explanation. The rate of reaction (14r) increases relative to that of (17r) with equivalence ratio due to the higher temperature and greater hydrogen atom concentration at blowout. Enhancement of (14r) relative to (17r) also occurs with mechanism III relative to mechanism I.

4.2 Summary

Argon and nitrogen acted as physical inhibitors affecting lower temperatures at blowout and increased residence times. Hydrogen bromide behaved like nitrogen for the artificial case of no hydrogen bromide kinetics. Hydrogen bromide addition resulted in increased oxygen consumption, increased blowout temperatures, increased residence times and reduced radical pool fractions. The parameter Θ_t employed to provide some indication of inhibition effectiveness was a more reasonable choice to characterize argon and nitrogen inhibition but exhibited large variations with composition for hydrogen bromide inhibition. Using Θ_t as an indicator of inhibitor effectiveness revealed that hydrogen bromide was the most effective and argon the least. Hydrogen bromide was found to be more effective at high pressures than low, for mechanism III relative to mechanism I, and for rich over stoichiometric and lean flames. The hydrogen bromide reactions important to inhibition are reactions (14r) and (17r), with the former the more important of the two. The effectiveness of hydrogen bromide resulted in a complex trade-off between reaction exothermicity and radical scavenging ability.

REFERENCES

1. Halogenated Fire Suppressants, ACS Symposium Series 16, (R.G. Gann, Editor), 1975.

2. Friedman, R. and Levy, J.B., Wright Air Development Center Technical Report 56-568, AD No. 110685, January 1957.

3. Creitz, E.C., J. Res. Nat. Bur. Stand. 74A, p. 521, 1970.

4. Hastie, J.W., J. Res. Nat. Bur. Stand. 77A, p. 733, 1973.

5. Jones, A. and Prothero, A., Comb. and Flame 12, 457, 1968.

6. Pratt, D.T. and Bowman, B.R., "A PSR-A Computer Program for Calculation of Combustion Reactions Kinetics in a Macromixed Perfectly Stirred Reactor," Circular 43, Engineering Extension Service, Washington State University, Pullman, Washington, 1972.

7. Baulch, D.L., Drysdale, D.D., Horne, D.G., and Lloyd, A.C., Evaluated Kinetic Data for High Temperature Reactions, Butterworths, London, 1972.

8. Baulch, D.L. Drysdale, D.D., and Horne, D.G., Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 107, 1973.

9. Wilson, W.E.,Jr., J. Chem. Ref. Data 1., 535, 1972.

10. Myerson, A.L. and Watt, W.D., J. Chem. Phys. 49, 425, 1968.

11. Johnston, H.S., "Gas Phase Reaction Kinetics of Neutral Oxygen Species," NSRDS-NBS 20, 1968.

12. Lloyd, A.C., Int. J. Chem. Kinetics 6, 169, 1974.

13. Vidal, C., J. Chem. Phys. 68, 1360, 1971.

14. Brown, N.J., ACS Symposium Series 16, 341, 1975.

15. MacDonald, R.G., and Burns, G., J. Chem. Phys. 66, 3598, 1977.

16. Cohen, N., Giedt, R.R., and Jacobs, T.A., Int. J. Chem. Kinet. 5, 425, 1973.

17. Fristrom, R.M. and Sawyer, R.F., AGARD Conference Proceedings No. 84 on Aircraft Fuels and Lubricants, and Fire Safety, AGARD-CP-84-71, Section 12, North Atlantic Treaty Organization, 1971.

18. Larsen, E.R., ACS Symposium Series 16, 376, 1975.

19. Dixon-Lewis, G. and Simpson, R.J., Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1111, 1976.

20. Rosser, W.A., Wise, H., and Miller, J., Seventh Symposium (International) on Combustion, Butterworth Scientific Publications, London, 175, 1959.

21. Fristrom, R.M. and Van Tiggelen, P., Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 773, 1978.

LIST OF TABLES

Table I. Kinetic Data for the $H_2/O_2/Ar/HBr$ System.

Table II. Summary of Ar Inhibition in a Stoichiometric $H_2/O_2/Ar$ Mixture.

Table III. Summary of N_2 Inhibition in a Stoichiometric $H_2/O_2/Ar$ Mixture.

Table IV. Summary of HBr Inhibition in a Lean $H_2/O_2/Ar$ Mixture.

Table V. Summary of HBr Inhibition in a Stoichiometric $H_2/O_2/Ar$ Mixture.

Table VI. Summary of HBr Inhibition in a Rich $H_2/O_2/Ar$ Mixture.

Table VII. Summary of the Effects of Rate Coefficient Variation on HBr Inhibition.

LIST OF FIGURES

Figure 1. Blowout residence time as a function of equivalence ratio for $H_2/O_2/Ar$ mixtures at 10^{-2} atmospheres.

Figure 2. Blowout residence time as a function of equivalence ratio for $H_2/O_2/Ar$ mixtures at 1.0 atmosphere.

Figure 3. Radical pool fraction as a function of residence time for 2 and 10 mole percent additional Ar for stoichiometric $H_2/O_2/Ar$ mixtures reacting via mechanism I at 10^{-2} atmospheres.

Figure 4. Radical pool fraction as a funciton of residence time for 2 and 0 mole percent HBr for stoichiometric $H_2/O_2/Ar$ mixtures reacting via mechanism I at 10^{-2} atmospheres.

Figure 5. Radical pool fraction as a function of residence time for 2 and 10 mole percent HBr for stoichiometric $H_2/O_2/Ar$ mixtures reacting via mechanism I at one atmosphere.

Figure 6. Radical pool fraction as a function of residence time for 2 and 10 mole percent HBr for rich $H_2/O_2/Ar$ mixtures reacting via mechanism I at one atmosphere.

Figure 7. Radical pool fraction as a function of residence time for 2 and 8 mole percent HBr for lean $H_2/O_2/Ar$ mixtures reacting via mechanisms I and III at one atmoshpere.

Figure 8. Residence time versus inhibitor mole fraction for Ar, N_2, and HBr for stoichiometric $H_2/O_2/Ar$ mixtures reacting via mechanism I at 10^{-2} atmosphere.

Figure 9. Residence time versus inhibitor mole fraction for Ar, N_2, and HBr for stoichiometric $H_2/O_2/Ar$ mixtures reacting via mechanism I at 1.0 atmosphere.

TABLE I

$H_2/O_2/Ar/HBr$ Kinetics

$$k = 10^{B_j} T^{N_j} \exp(-E_j/RT)(cm^3/mole)^{m-1} sec^{-1}$$

Reaction	B_j	N_j	E_j(cal/mole)	Ref.
1) $O + H_2 \rightarrow OH + H$	10.26	1.0	8900	8
2) $OH + H_2 \rightarrow H + H_2O$	13.36	0.0	5200	9
3) $H + O_2 \rightarrow OH + O$	14.34	0.0	16790	7
4) $OH + OH \rightarrow O + H_2O$	12.80	0.0	1093	7
5) $H_2 + M \rightarrow 2H + M$	12.35	0.5	92600	10
6) $H + OH + M \rightarrow H_2O + M$	21.92	-2.0	0	7
7) $O + O + M \rightarrow O_2 + M$	17.11	-1.0	341	11
8) $H + O_2 + M \rightarrow HO_2 + M$	15.18	0.0	-1000	7
9) $HO_2 + H \rightarrow 2OH$	14.40	0.0	1900	7
10) $OH + HO_2 \rightarrow H_2O + O_2$	13.70	0.0	1000	12
11) $O + HO_2 \rightarrow OH + O_2$	13.70	0.0	1000	12
12) $H + HO_2 \rightarrow H_2O + O$	13.70	0.0	1000	12
13) $H + HO_2 \rightarrow H_2 + O_2$	13.40	0.0	700	12
14) $Br + H_2 \rightarrow HBr + H$	14.13	0.0	18400	13
15) $H + Br_2 \rightarrow HBr + Br$	14.53	0.0	903	14
16) $Br + Br + M \rightarrow Br_2 + M$	18.86	-1.42	0	15
17) $HBr + M \rightarrow H + Br + M$	21.78	-2.0	88000	16

*reverse rate coefficients are determined from forward values and equilibrium constants

m ≡ order of the reaction

TABLE II[a]
Ar Inhibition

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O_2(moles)[b]	θ_t
Ar	0.0	1.0	10^{-2}	I	9.11×10^{-3}	870	.234	-
	0.02				9.47×10^{-3}	869	.236	.15
	0.04				9.85×10^{-3}	868	.236	.14
	0.06				10.25×10^{-3}	868	.238	.13
	0.08				10.69×10^{-3}	867	.238	.13
	0.10				11.15×10^{-3}	866	.238	.13
Ar	0.0	1.0	10^{-2}	III	8.46×10^{-3}	871	.231	-
	0.02				8.79×10^{-3}	872	.232	.14
	0.04				9.14×10^{-3}	870	.232	.14
	0.06				9.52×10^{-3}	869	.233	.14
	0.08				9.92×10^{-3}	868	.234	.13
	0.10				10.35×10^{-3}	868	.236	.13
Ar	0.00	1.0	1.0	I	1.80×10^{-5}	1129	.252	-
	0.02				1.88×10^{-5}	1128	.253	.18
	0.04				1.96×10^{-5}	1126	.253	.17
	0.06				2.05×10^{-5}	1125	.255	.16
	0.08				2.15×10^{-5}	1124	.256	.16
	0.10				2.25×10^{-5}	1123	.258	.16
Ar	0.00	1.0	1.0	III	1.37×10^{-5}	1138	.237	-
	0.02				1.42×10^{-5}	1137	.238	.14
	0.04				1.49×10^{-5}	1135	.240	.15
	0.06				1.56×10^{-5}	1134	.241	.15
	0.08				1.63×10^{-5}	1132	.242	.15
	0.10				1.71×10^{-5}	1131	.244	.15

a) Standard mix: 1.0 mole H_2, 0.5 mole O_2, 1.5 mole Ar. Additional Ar is added to dilute standard mix by initial mole fractions tabulated.

b) Moles of O_2 consumed out of a possible 0.5 moles.

TABLE III

N_2 Inhibition

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O_2(moles)[b]	θ_t
N_2	0.00	1.0	10^{-2}	I	9.11×10^{-3}	870	.234	-
	0.02				9.55×10^{-3}	868	.234	.18
	0.04				10.00×10^{-3}	867	.236	.17
	0.06				10.50×10^{-3}	866	.239	.16
	0.08				11.00×10^{-3}	865	.240	.16
	0.10				11.60×10^{-3}	864	.240	.15
N_2	0.00	1.0	10^{-2}	III	8.46×10^{-3}	871	.231	-
	0.02				8.86×10^{-3}	871	.233	.17
	0.04				9.29×10^{-3}	869	.233	.17
	0.06				9.75×10^{-3}	868	.235	.16
	0.08				10.25×10^{-3}	867	.236	.16
	0.10				10.78×10^{-3}	866	.238	.15
N_2	0.00	1.0	1.0	I	1.80×10^{-5}	1129	.252	-
	0.02				1.90×10^{-5}	1127	.253	.22
	0.04				2.00×10^{-5}	1126	.255	.20
	0.06				2.11×10^{-5}	1124	.257	.20
	0.08				2.24×10^{-5}	1122	.259	.19
	0.10				2.38×10^{-5}	1120	.261	.19
N_2	0.00	1.0	1.0	III	1.37×10^{-5}	1138	.237	-
	0.02				1.44×10^{-5}	1136	.239	.19
	0.04				1.52×10^{-5}	1134	.241	.19
	0.06				1.61×10^{-5}	1132	.243	.19
	0.08				1.70×10^{-5}	1130	.244	.18
	0.10				1.81×10^{-5}	1128	.247	.18

[a] Standard mix: 1.0 mole H_2, 0.5 mole O_2, 1.5 moles Ar. Additional N_2 is added to give indicated mole fraction.

[b] Moles O_2 consumed out of a possible 0.5 moles.

TABLE IV[a]

HBr Inhibition at a 0.5 Equivalence Ratio

Inhibitor	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O_2(moles)[b]	θ_t
HBr	0.00	0.5	10^{-2}	I	11.50×10^{-3}	828	.268	-
	0.02				12.00×10^{-3}	842	.295	.14
	0.06				12.80×10^{-3}	874	.350	.14
	0.10				13.00×10^{-3}	913	.408	.11
HBr	0.00	0.5	10^{-2}	III	9.84×10^{-3}	862	.297	-
	0.02				10.30×10^{-3}	851	.293	.16
	0.06				11.10×10^{-3}	885	.349	.16
	0.10				11.90×10^{-3}	913	.392	.15
HBr	0.00	0.5	1.0	I	2.33×10^{-5}	1060	.299	-
	0.02				2.44×10^{-5}	1089	.331	.18
	0.04				2.56×10^{-5}	1120	.357	.19
	0.06				2.70×10^{-5}	1155	.387	.21
	0.08				2.86×10^{-5}	1198	.420	.22
HBr	0.00	0.5	1.0	III	1.41×10^{-5}	1102	.288	-
	0.02				1.58×10^{-5}	1140	.323	.43
	0.04				1.79×10^{-5}	1172	.356	.45
	0.06				2.01×10^{-5}	1208	.389	.46
	0.08				2.28×10^{-5}	1248	.423	.46

a) Standard mix: 1.0 mole H_2, 1.0 mole O_2; 2.0 mole Ar. Inhibitor added to give indicated mole fraction.

b) O_2 moles consumed out of a possible 1.0 moles.

TABLE V[a]

HBr Inhibition in a Stoichiometric Flame

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O_2(moles)[b]	θ_t
HBr	0.00	1.0	10^{-2}	I	9.11×10^{-3}	870	.234	-
	0.02				9.58×10^{-3}	884	.254	.20
	0.04				10.00×10^{-3}	900	.273	.19
	0.06				10.40×10^{-3}	918	.293	.19
	0.08				10.90×10^{-3}	937	.311	.20
	0.10				11.35×10^{-3}	960	.332	.20
HBr	0.00	1.0	10^{-2}	III	8.46×10^{-3}	871	.231	-
	0.02				8.93×10^{-3}	888	.251	.22
	0.04				9.39×10^{-3}	904	.270	.21
	0.06				9.88×10^{-3}	945	.312	.23
	0.08				10.30×10^{-3}	954	.322	.22
	0.10				10.80×10^{-3}	964	.330	.21
HBr	0.00	1.0	1.0	I	1.80×10^{-5}	1129	.252	-
	0.02				1.91×10^{-5}	1158	.271	.26
	0.04				2.04×10^{-5}	1192	.292	.27
	0.06				2.22×10^{-5}	1226	.312	.31
	0.08				2.45×10^{-5}	1267	.333	.34
	0.10				2.80×10^{-5}	1313	.356	.38
HBr	0.00	1.0	1.0	III	1.37×10^{-5}	1138	.237	-
	0.02				1.51×10^{-5}	1173	.261	.40
	0.04				1.69×10^{-5}	1208	.284	.43
	0.06				1.90×10^{-5}	1244	.307	.45
	0.08				2.17×10^{-5}	1286	.330	.47

a) Standard mix: 1.0 mole H_2, 0.5 moles O_2, 1.5 moles Ar. Inhibitor added to give indicated mole fraction.

b) O_2 mole consumed out of a possible 0.5 moles.

TABLE VI[a]

HBr Inhibition in a 1.5 Equivalence Ratio Flame

INHIBITOR	CONCENTRATION (mole fraction)	ϕ	P(atm)	Mech.	t(sec)	T(K)	O_2(moles)[b]	θ_t
HBr	0.00	1.5	10^{-2}	I	10.50×10^{-3}	889	.213	-
	0.02				11.56×10^{-3}	903	.226	.38
	0.04				12.79×10^{-3}	919	.238	.38
	0.06				14.38×10^{-3}	935	.250	.40
	0.08				16.56×10^{-3}	954	.262	.41
	0.10				19.87×10^{-3}	976	.272	.47
HBr	0.00	1.5	10^{-2}	III	10.10×10^{-3}	888	.209	-
	0.02				11.11×10^{-3}	904	.223	.37
	0.04				12.34×10^{-3}	919	.237	.39
	0.06				13.93×10^{-3}	935	.248	.40
	0.08				16.11×10^{-3}	954	.260	.42
	0.10				19.44×10^{-3}	977	.271	.44
HBr	0.00	1.5	1.0	I	2.19×10^{-5}	1150	.221	-
	0.02				2.47×10^{-5}	1188	.234	.49
	0.04				2.87×10^{-5}	1223	.247	.53
	0.06				3.51×10^{-5}	1264	.261	.58
	0.08				4.71×10^{-5}	1313	.274	.63
	0.10				7.64×10^{-5}	1385	.288	.69
HBr	0.00	1.5	1.0	III	1.82×10^{-5}	1152	.209	-
	0.02				2.13×10^{-5}	1188	.226	.60
	0.04				2.55×10^{-5}	1226	.241	.62
	0.06				3.22×10^{-5}	1269	.257	.66
	0.10				7.42×10^{-5}	1394	.288	.73

a) Standard mix: 1.0 mole H_2, .33 moles O_2, 1.33 moles Ar. Inhibitor added to give indicated mole fraction.

b) O_2 moles consumed out of a possible 0.33 moles.

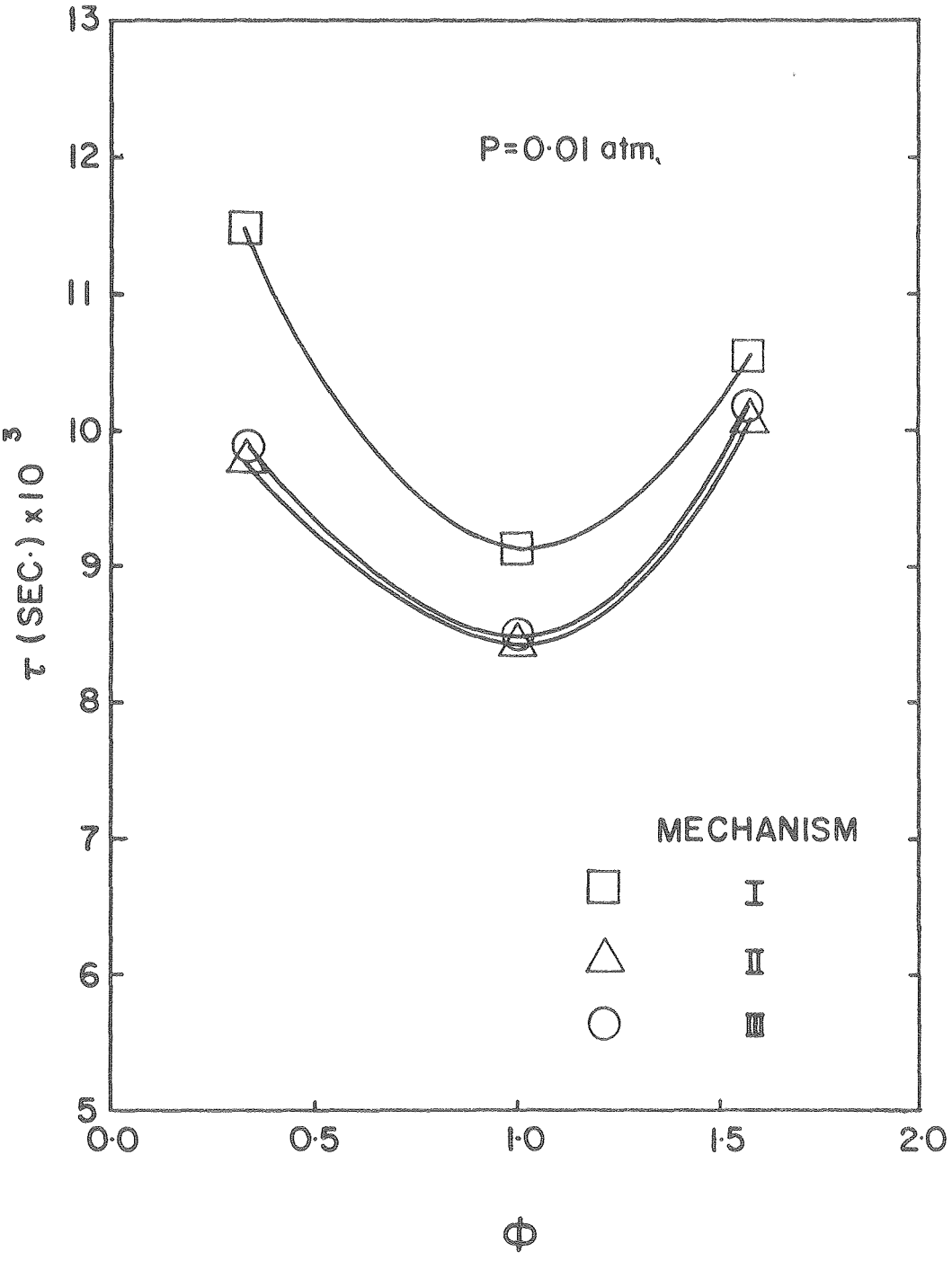
TABLE VII[a]

Effect of Rate Coefficient Variation

Case	HBr Concentration (mole fraction)	t(sec)	T(K)	O_2(moles)[b]	θ_t
A	0.00	1.80×10^{-5}	1129	.252	—
	0.02	1.91×10^{-5}	1158	.271	.26
	0.04	2.04×10^{-5}	1192	.292	.27
	0.06	2.22×10^{-5}	1226	.312	.31
	0.08	2.45×10^{-5}	1267	.333	.34
	0.10	2.80×10^{-5}	1313	.356	.38
B	0.00	1.80×10^{-5}	1129	.252	—
	0.02	2.04×10^{-5}	1143	.271	.52
	0.04	2.33×10^{-5}	1158	.290	.53
	0.06	2.69×10^{-5}	1174	.312	.54
	0.08	3.15×10^{-5}	1186	.331	.54
	0.10	3.76×10^{-5}	1203	.352	.55
C	0.00	1.80×10^{-5}	1129	.252	—
	0.02	$.82 \times 10^{-5}$	1516	.294	
	0.04	$.93 \times 10^{-5}$	1662	.323	
	0.06	1.19×10^{-5}	1765	.347	
	0.08	1.68×10^{-5}	1842	.368	
	0.10	2.51×10^{-5}	1892	.383	.32

a) Stoichiometric, atmospheric pressure mixture with HBr inhibition, reacting via mechanism I.

b) O_2 moles consumed out of a possible 0.5 moles.



XBL 784-7958

Figure 1

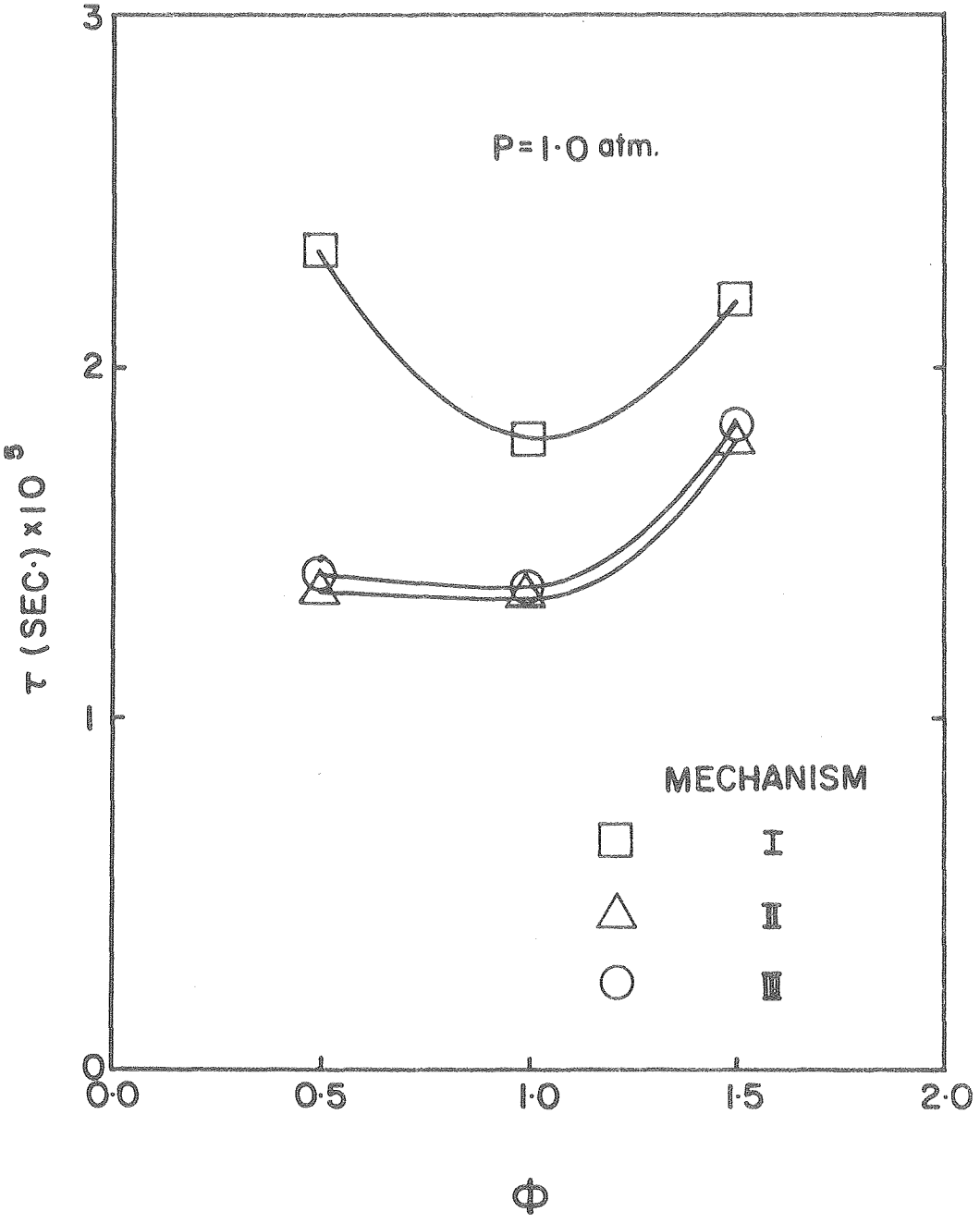
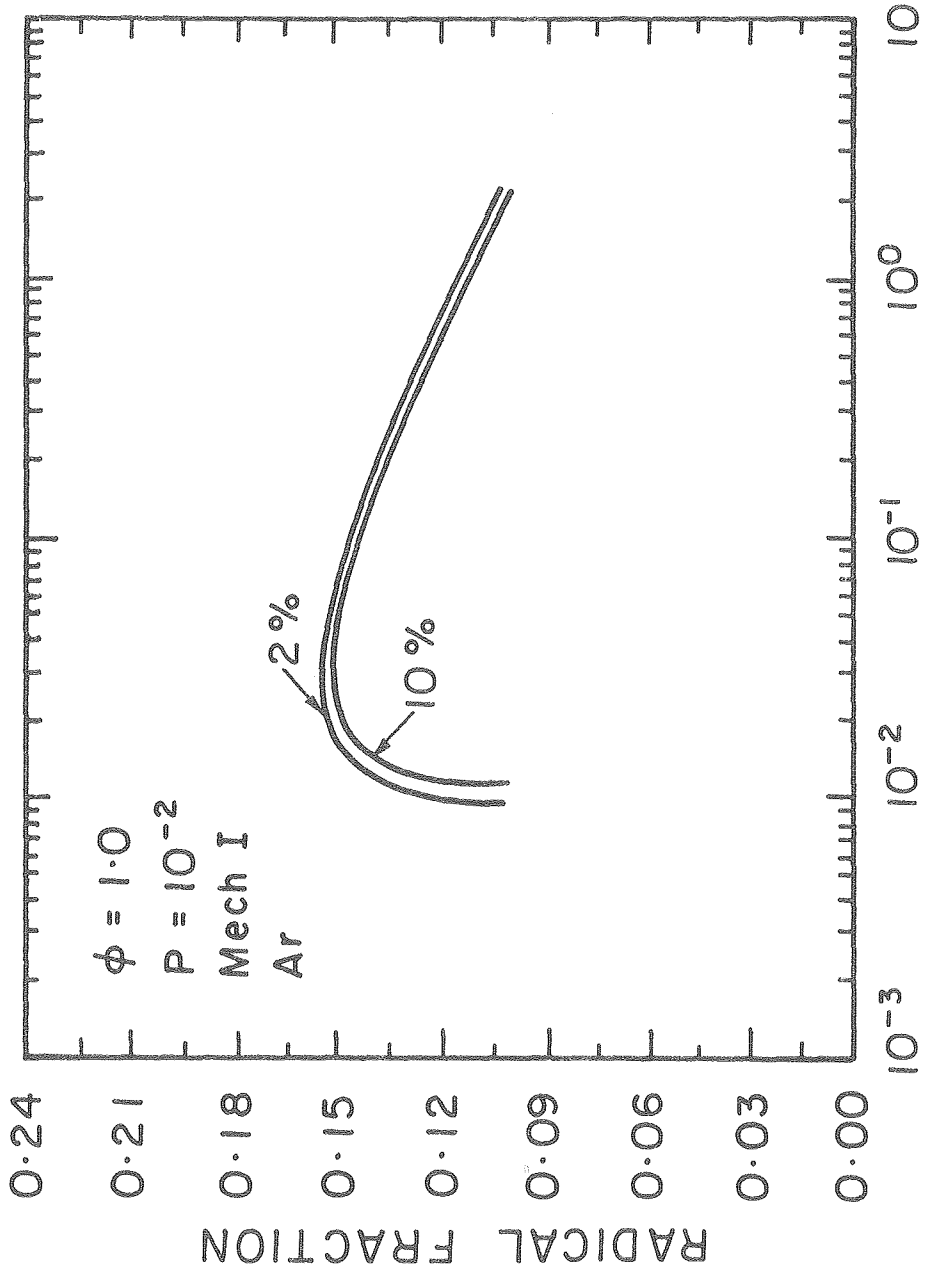
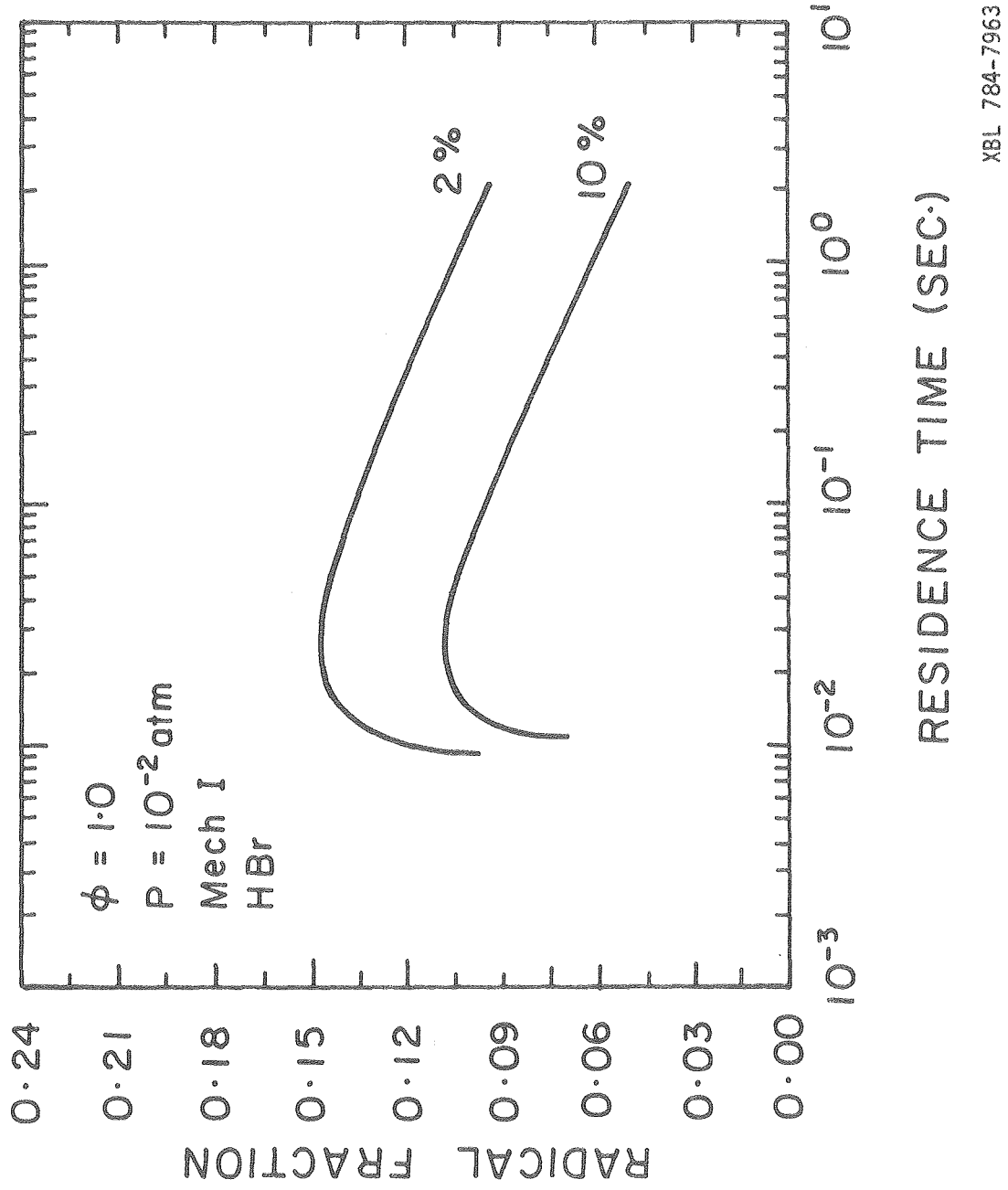

P = 1·0 atm.
τ (SEC.) x 10^5
3
2
1
0
0·0
0·5
1·0
1·5
2·0
Φ
MECHANISM
I
II
III
XBL 784-7959

Figure 2



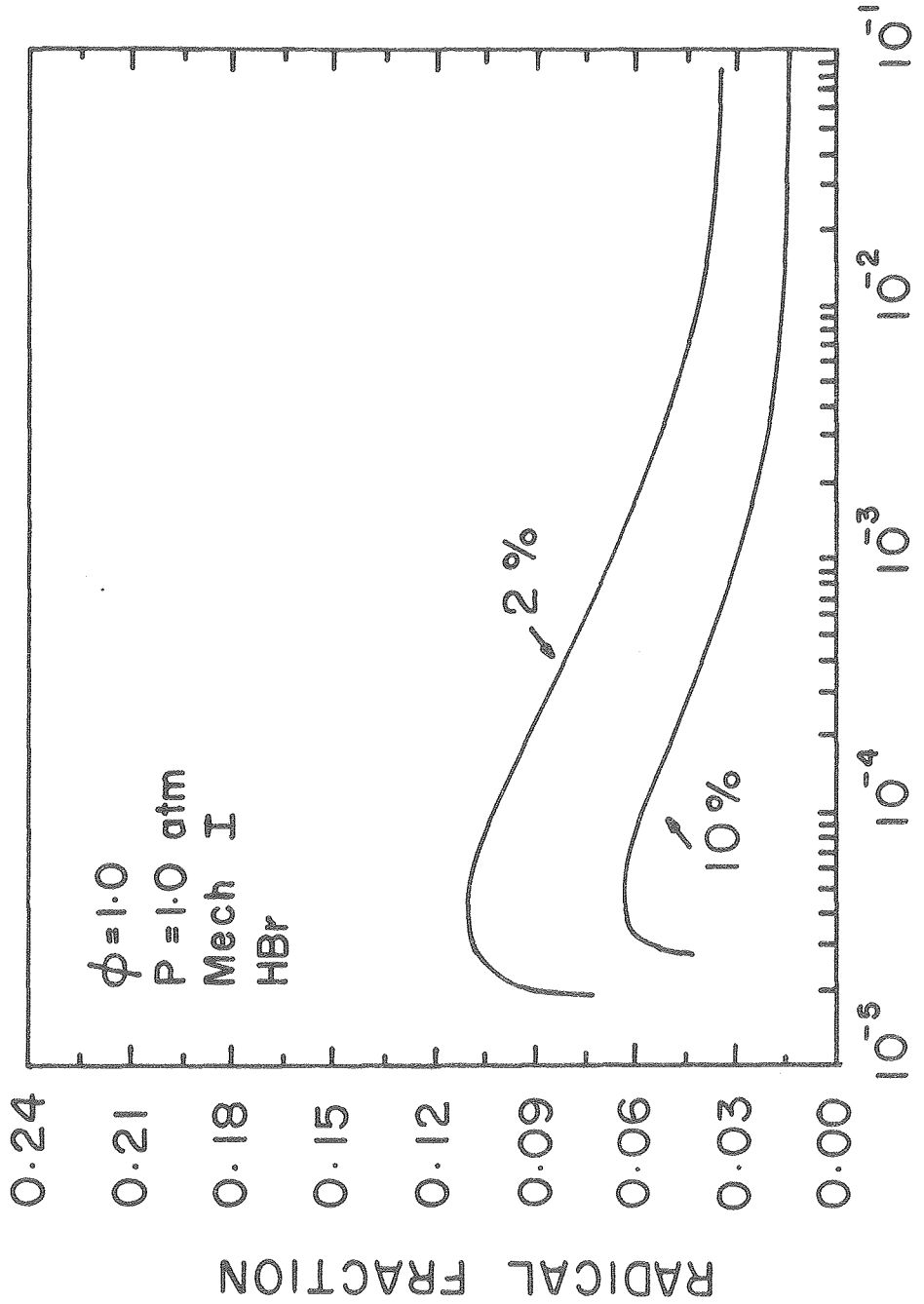
XBL 784-7964

Figure 3



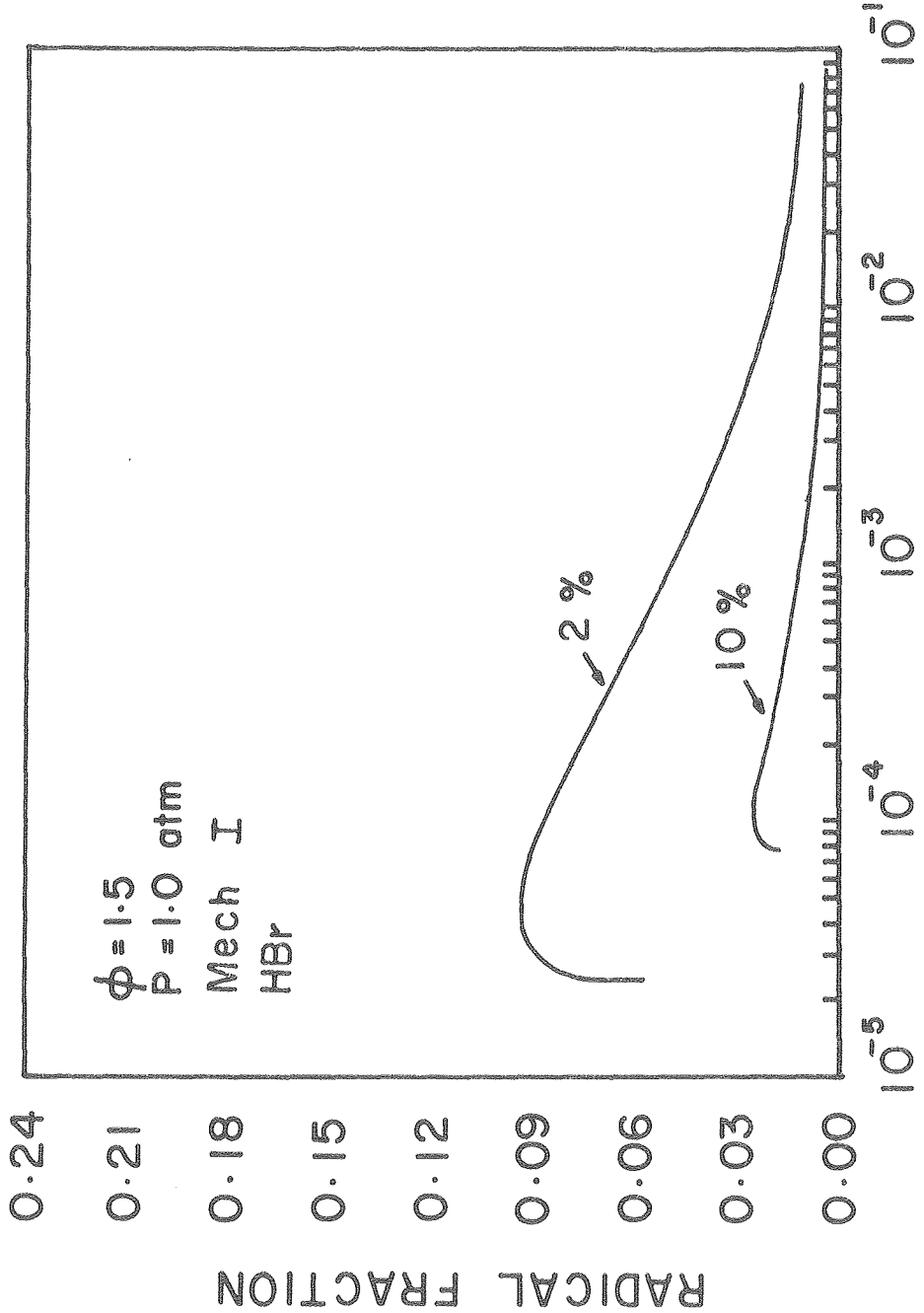
XBL 784-7963

Figure 4



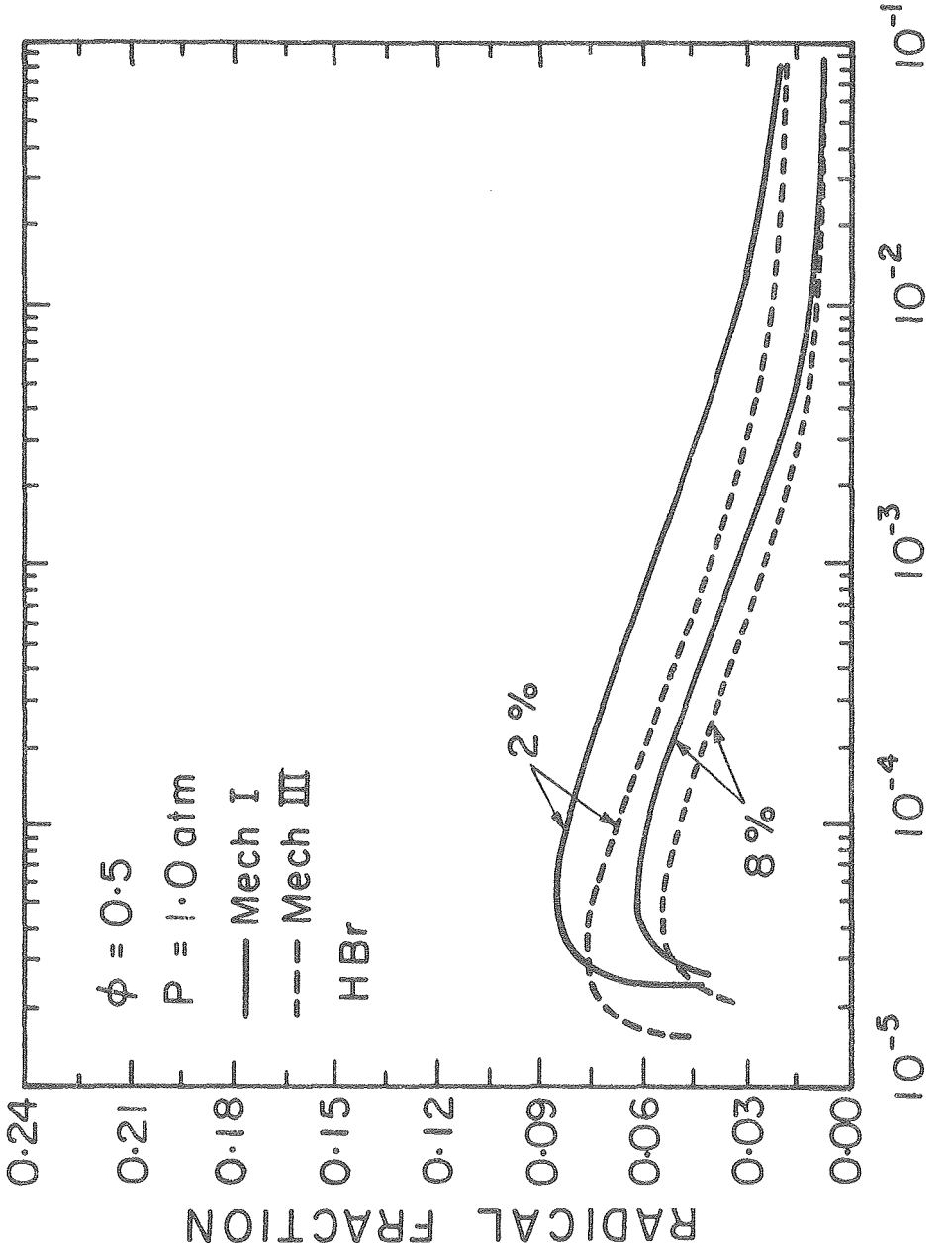
XBL 784-7966

Figure 5



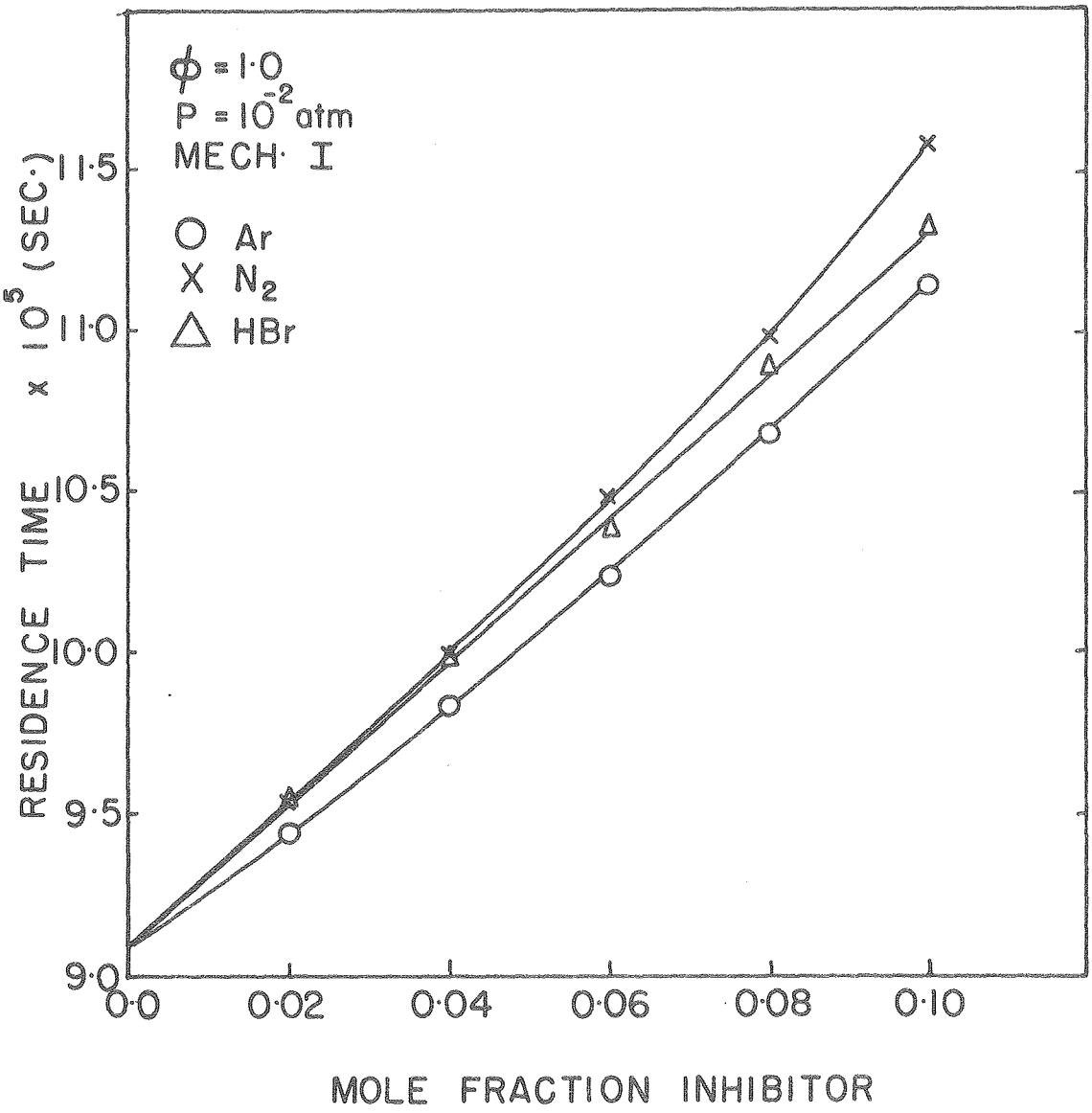
XBL 784-7965

Figure 6



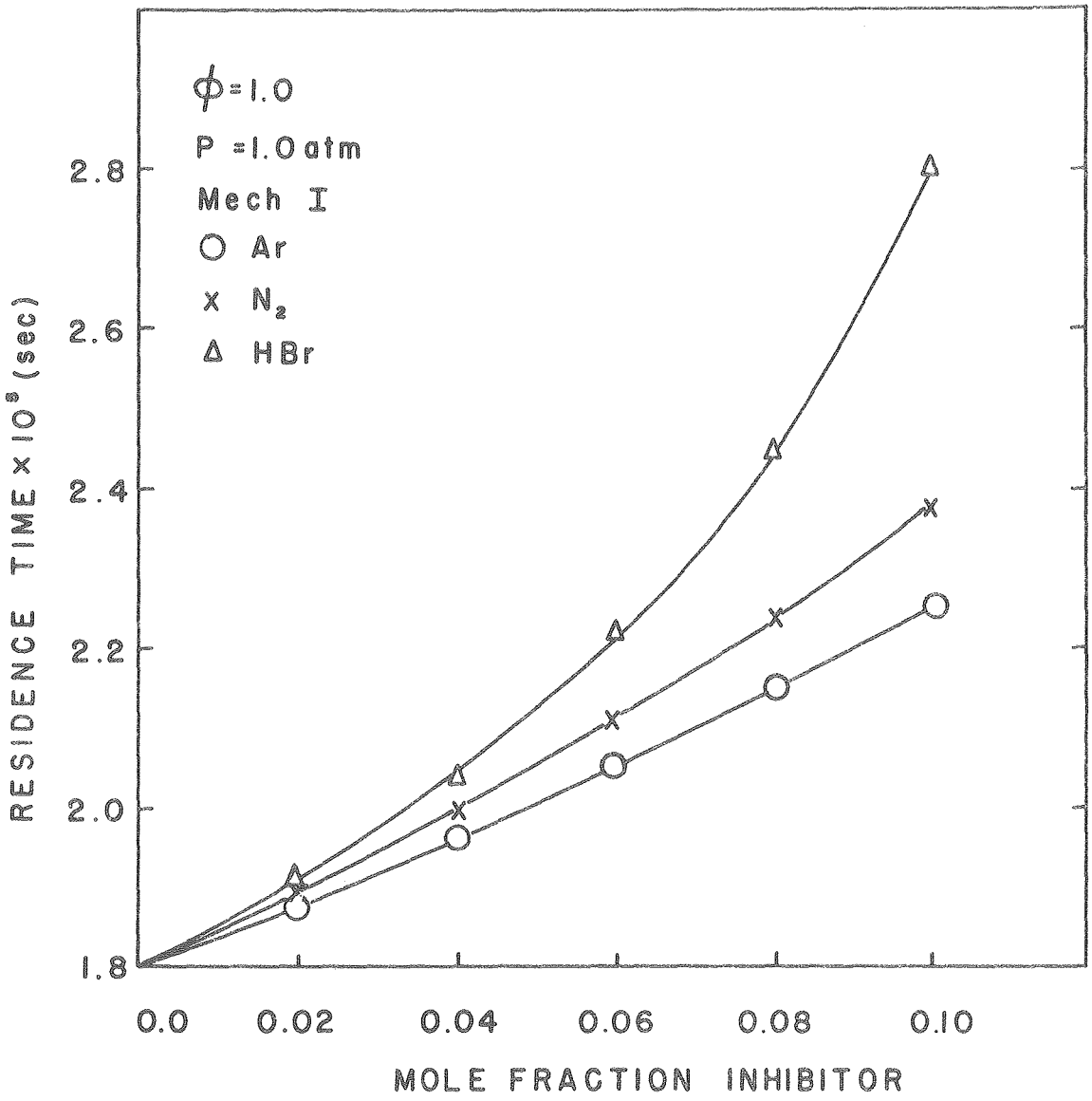
XBL 784-7962

Figure 7



XBL 784-7957

Figure 8



XBL 784-7960

Figure 9

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720